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Vapor-Phase Lubricants: Nanometer-Scale Mechanisms and Applications to Sub-micron and Rotating Machinery.

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11. SUPPLEMENTARY NOTES

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13. ABSTRACT ***(Maximum 200 Words)***

Vapor-phase lubricants: Nanometer-scale mechanisms and applications to sub-micron machinery was a new program supported by AFOSR involving a set of experimental seeking to explore the nanometer-scale origins of the lubricating properties of vapor-phase lubricants in controlled environmental conditions and well-defined contact geometries. Although such lubricants have been the subject of much research for over 40 years, the atomic-scale details of their lubrication mechanisms are far from being satisfactorily understood. We have evaporated high purity Fe and Cr substrates in UHV conditions onto Quartz Crystal Microbalances, and then measured the uptake rates of TCP in the temperature range 25-400 C. The Sample's surface chemistries were also investigated by means of Auger Spectroscopy, and, as expected, graphitic carbon was found to be the dominant surface constituent. More surprisingly, we observed the uptake rates to depend on sample history, providing positive confirmation that interdiffusion of TCP with Fe is extensive, and key to its beneficial tribological properties.

A second set of experiments has been motivated by the fact that vapor lubrication mechanisms may prove to be of critical importance to sub-micron mechanical systems on account of the difficulty of applying a lubricant to such systems by other techniques. These studies involve characterization of the nanotribological behaviors of simple organics and TBPP on metal surfaces in a simple nanomechanical system consisting of a STM tip sliding along the surface electrode of a QCM electrode. They have revealed that surface regions exposed to lubricants which directly experience rubbing exhibit lower friction and virtually no wear. The phenomenon is attributable to either tribochemically formed graphitic regions or heating induced migration of carbon to the interface.

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Final Technical Report

Vapor Phase Lubricants: Nanometer-scale Mechanisms and Applications to Sub-micron Machinery, Award # F49620-99-1-0006
Funding Period: 12/1/98 – 11/30/00

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(1) (2) Summary of Research Activities and Accomplishments

AFOSR#49620-99-1-0006 funded a set of experimental studies involving the nanometer-scale origins of the lubricating properties of vapor-phase lubricants in controlled environmental conditions and well-defined contact geometries. The goal of the first set of experiments was to verify and quantify at nanometer length-scales the fundamental mechanisms which are believed to underlie the lubricating properties of TBPP/iron, a system which is of current interest to the Air Force on account of its potential for lubricating in extreme temperature environments. Auger Spectroscopy, Quartz Crystal Microbalance (QCM) and Scanning Tunneling Microscopy (STM) measurements have been performed on the lubricant, as well as a number of control systems, at various stages of its formation on a pure iron surface.

A second set of experiments has been motivated by the fact that vapor lubrication mechanisms may prove to be of critical importance to sub-micron mechanical systems on account of the difficulty of applying a lubricant to such systems by other techniques. These studies involve characterization of the nanotribological behaviors of simple organics and TBPP on metal surfaces in a simple nanomechanical system consisting of a STM tip sliding along the surface electrode of a QCM electrode.

The work originally proposed for AFOSR#49620-99-0006 has been completed, and we are currently in the process of publishing all of the results. During the first year of funding at North Carolina State University (the PI was funded by AFOSR for one year at Northeastern University prior to the present grant), we designed and assembled an ultra-high vacuum system to house a state-of –the art RHK model 300 scanning tunneling microscope (funded through equipment grant #F49620-98-1-0237), which was added to an existing system. (Figure 1)

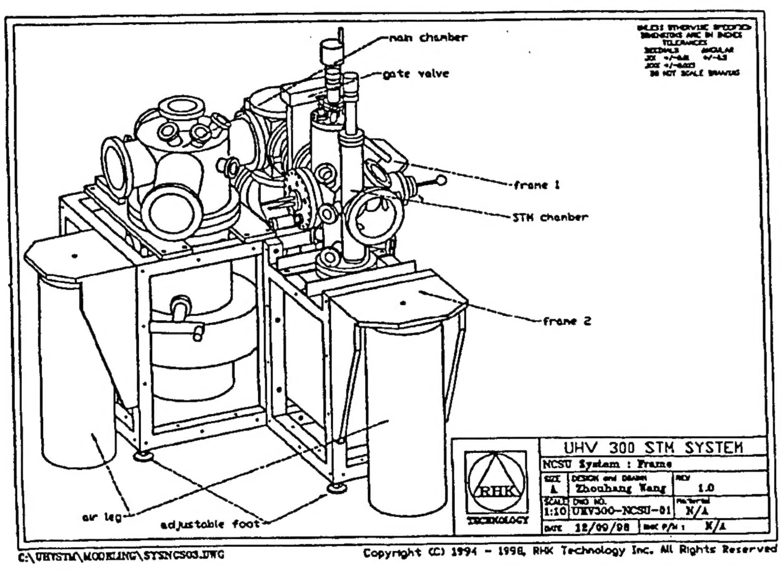


Figure 1. Schematic of the new additions to the existing chamber. The STM addition is now in place and the entire system has been mounted on vibration isolation legs.

Upon completion of the chamber modifications, the apparatus has been devoted entirely to research supported by AF49620-99-1-0006. Highlights of our accomplishments include:

- The nanometer scale mobilities of the vapor-phase lubricants TBP and TCPP have been explored, particularly how they spread on surfaces and diffuse into Fe and Cr substrates. Diffusion into and out of the bulk has been monitored directly for the first time with STM-QCM, an instrument that we have greatly perfected under current funding. (Figure 2)
- Positive confirmation of N. Forster's 1999 suggestion that diffusion of TCP and TBPP and their byproducts is extensive in iron substrates, and may well play a dominant role in its beneficial tribological behaviors. (Figures 3-5) We have observed a high degree of diffusion of both TCP and TBPP into iron, in stark contrast to the behavior observed for adsorption on Chrome.

- STM-QCM observations that the surface regions exposed to TCP and TBPP which directly experience rubbing (by means of an STM tip on a moving QCM surface at speeds exceeding 1 m/s) exhibit lower friction. In the upcoming period we propose to establish whether the rubbed , graphitic region forms on account of (1) a tribochemical reaction (2) heating-induced migration of carbon to the surface, or (3) wear of non-graphitic material. (Figure 6)

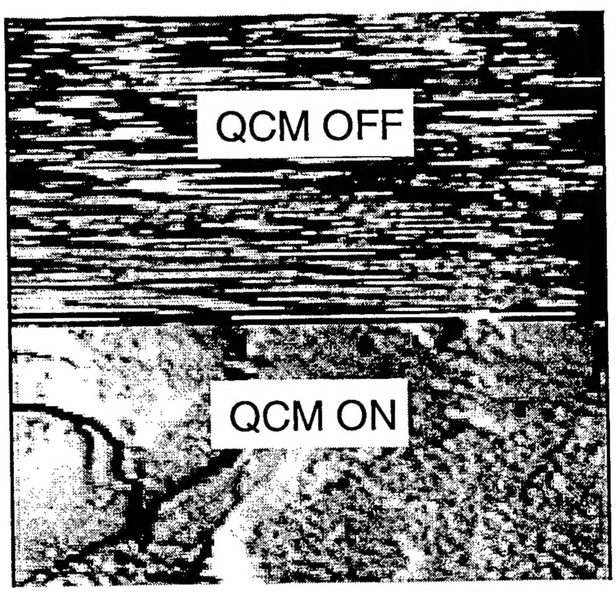


Figure 2. 350 nm x 350 nm image of a TBPP-lubricated surface at room temperature. The rubbing action of the vibrating QCM electrode against the STM tip is required to produce a stable image. The rubbing pushes aside the lubricant, forming holes through which the surface may be imaged. These holes fill-in with additional lubricant once the QCM is turned off or the tip is moved away from the region, indicating that the TBPP film is mobile at room temperature, demonstrating the importance of characterizing lubricant dynamics as well as chemical composition.

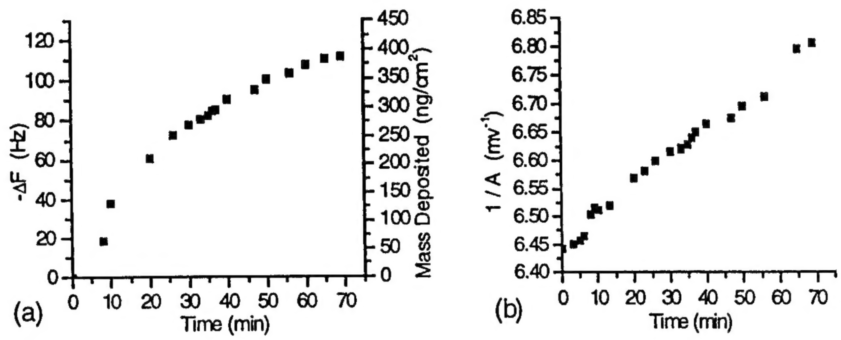


Figure 3. Uptake of TBPP on iron: The frequency, *F*, drop indicates mass adsorption. Shifts in amplitude, *A*, are related to adsorbate motion, both slippage and/or internal molecular motion of the adsorbed species. If such motions were not present, the amplitude shifts would be zero. Surprisingly, the uptake rate returns to its t = 0 value when the sample is left for a day with no exposure to further TBPP, even though the TBPP is not observed to desorb from the surface. This is due to the slow diffusion of the TBPP or fragments thereof into the iron substrate.

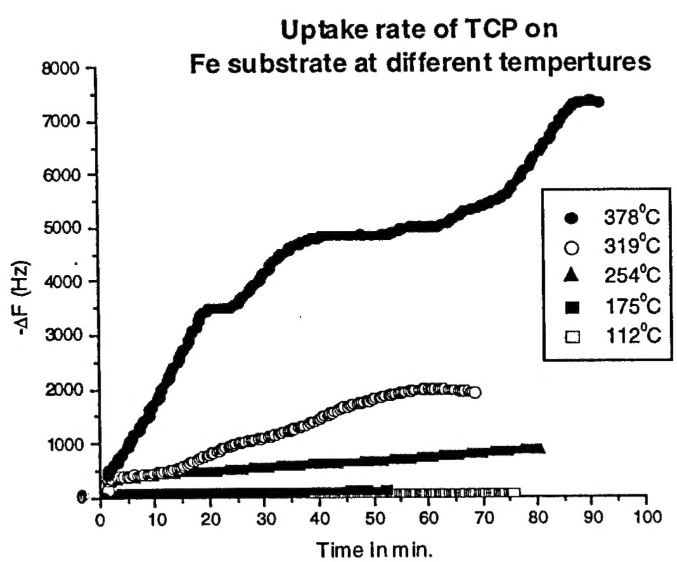
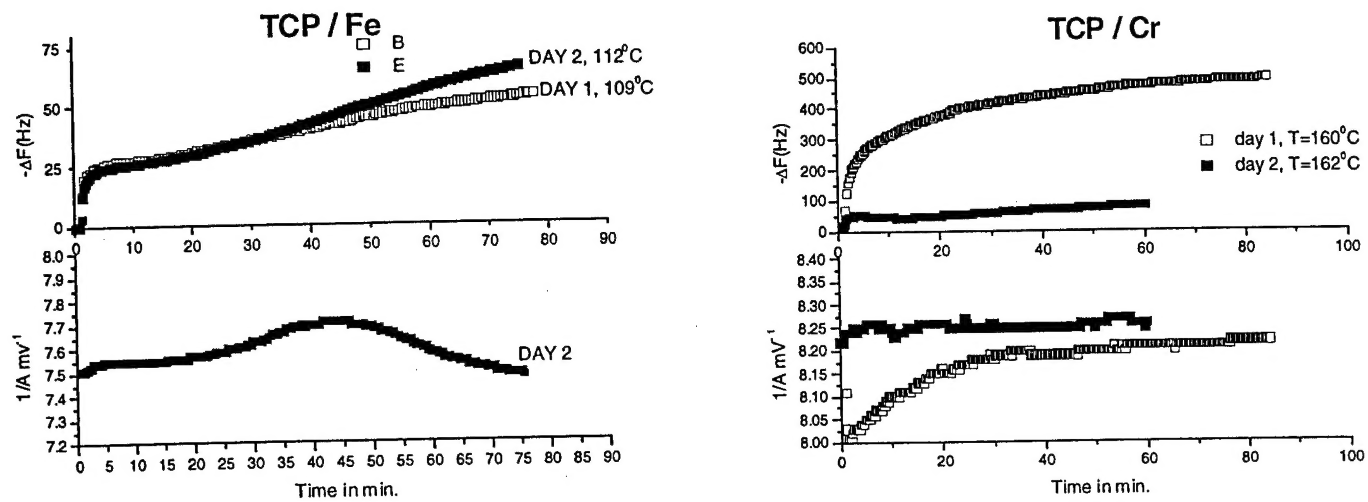


Figure 4. Uptake of TCP on pure iron (A frequency shift of 27 Hz corresponds to one molecular layer) at varying temperatures at a function of time. After long exposure, the iron film's ability to absorb TCP saturates. Future work is proposed to explore which factors determine the saturation level.



(a) (b)

Figure 5. Uptake of TCP on two successive days for (a) Iron and (b) Chrome surfaces. The iron surface continues to exhibit adsorption after a day-long wait while the chrome surface does not, indicative of the slow, but progressive manner in which the lubricant diffuses into iron.

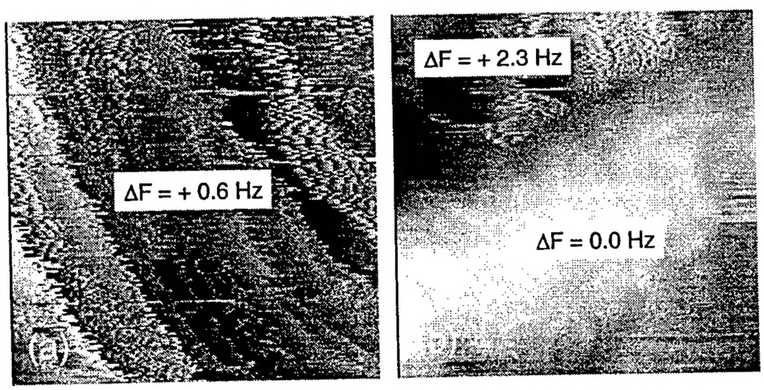


Figure 6. 70 nm × 70 nm STM images of a TBPP-lubricated surface after annealing to disassociate the TBBP molecules. QCM frequency shifts upon establishing tunneling contact in different regions are shown in boxes. Image (a) shows a non-rubbed region. Image (b) shows the same region after a rubbing period of a few minutes, during which the QCM was vibrating with the tip engaged in tunneling contact. Non-rubbed regions have a fringed appearance, indicative of residual molecular motion, and are accompanied by a small positive frequency shift when the tip is first engaged in tunneling. Rubbed regions have a more uniform appearance and exhibit no frequency shift when tunneling. The electrical properties of the tunneling junction suggest that the lubricant film is not simply worn away by rubbing, suggesting a tribochemical reaction associated with the interfacial sliding conditions achieved by the STM-QCM.

(3)Consultations/Technology Transitions

The work performed was carried out in close coordination with N. H. Forster at Wright-Patterson AFB, OH. Preliminary and final results were immediately conveyed to Forster, in order to speed the intermediate steps before introducing the technology into high speed rolling element bearings intended for use in gas turbine engines. The work was summarized at the June 1998 and June 1999 AFOSR/ONR/NSF tribology workshops, where Krim was able to closely consult on the project with AFOSR-funded A. Gellman and Forster. The researchers (Gellman, Krim and Forster) also met at Wright-Patterson AFB in August 1999 and at NCState University in November 1999. Krim and Forster met again at Wright-Patterson AFB in November 2000. The MEMS-related work is being performed in close collaboration with groups who fabricate micromechanical switches, and is coordinated with related efforts by M. Dugger at Sandia National Laboratories, and on AFOSR funded devices developed by P. Franzon at NCSU.

(4) Personnel Supported

Graduate students: Mohammed Abdelmaksoud (full time, Ph.D. on track for May 2001) and Tonya Coffey (supported by a GAANN fellowship, but working on AFOSR-related research); Jacqueline Krim (1 mo summer); Post-Doc: Brian Borovsky (full time); Lucas Wagner (undergrad physics major) (10 hours/week)

(5) Invited talks at conferences including the results of AFOSR support: (20)

Gordon Conference on *Chemistry at Interfaces*, (July 1998); 14th Int. Vacuum Congress/10th Int. Conf. Solid Surfaces/5th Int. Conference on *Nanometer Scale Sci.& Technol/* 10th Int. Conf. Quant. Surf. Analysis, Birmingham, UK, (Sept. 1998); American Vacuum Society National Symposium, *Topical Conference on the Science of MEMS*, Baltimore, MD, (Nov. 1998); American Vacuum Society National Symposium, *Job Information Forum* speaker, representing academia, Baltimore, MD, (Nov. 1998); Triangle Area Meeting of the Materials Research Society, Research Triangle Park, North Carolina, (November, 1998); American Chemical Society, *Fundamental Studies of Molecular Tribology Symposium*, Anaheim, CA, (March 1998); Materials Research Society Symposium on *Tribology*, San Francisco, CA, (June 1998); Gordon Research Conference on *Dynamics at Surfaces*, Andover, NH, (August 1998); *Complex Fluid Interfaces*, Pisa, Italy, (Sept. 1999); *Acoustic Wave Sensor Workshop*, Wasserburg, Germany, (Sept. 1999); *Dynamics Days 2000*, Los Alamos, NM, (Jan. 2000) American Chemical Society, *Symposium on Highlights in Chemistry in the 21st Century*, San Francisco, CA ,(March 2000); *Nanotribology: Research Opportunities*, March (2000) Joint Israel-North Carolina *Workshop on MEMS*, Haifa, Israel, (May 2000); 14th Symposium on Thermophysical Properties, *Liquids at Interfaces*, Boulder, CO, (June 2000); Material Research Society Symposium P on *Growth, Evolution and Properties of Surfaces*, Boston, MA, (Nov. 2000); VII International Summer School, ''Nicolas Cabrera" on *Imaging and Manipulation of Matter at the Nanometer Scale* , Madrid, Spain, (Sep. 2000); 8th Foresight Conference on *Molecular Nanotechnology*, Bethesda, MD, (Nov. 2000)

Invited seminars and colloquia including the results of AFOSR support: (21)

University of Maryland, Baltimore (Feb. 1998); Wayne State University, OH (Feb. 1998); University of Virginia, Charlottesville, VA (Mar. 1998); Holyoke College/Five College Lecturer, Holyoke, MA (April 1998); US Army, Natick Research Base, Natick, MA (May 1998); Northeastern University, Boston, MA (May 1998); Massachusetts Institute of Technology, Cambridge, MA (May 1998); Rutgers University, Piscataway, NJ (Oct. 1998); Meredeth College, Raleigh, NC (Oct. 1998); Lawrence Berkeley Laboratory, UC Berkeley Berkeley, CA (Dec. 1998); University of New Mexico, Albuquerque, NM (Dec. 1998); University of Chicago, Chicago, IL (Jan. 1999); University of Illinois, Carbondale (Jan. 1999); Duke University, Durham, NC (Feb. 1999); Clemson University, SC (Feb. 1999); McMaster University, Ontario, Canada (March 1999); University of Waterloo, Ontario, Canada (March 1999); University of North Carolina, Wilmington (April 1999); University of Wisconsin, Milwaukee, (Dec. 1999); University of North Carolina, Chapel Hill (Jan. 2000); Weizmann Institute, Israel (May, 2000); Wake Forest University, Winston-Salem, NC (Oct. 2000)

Contributed Presentations including the results of AFOSR support: (7)
Vapor-Phase Lubricants: Nanometer Scale Mechanisms and Applications to Sub-micron Machinery, M. Abdelmaksoud, at the 1999 AVS National Symposium; QCM-STM Studies of Vapor-deposited Films on Metals, B. Borovsky, at the1999AVS National Symposium; Adhesion Properties of Gold-on-Gold Microswitch Contacts, S. Majumbder, N.E. McGruer, P.A. Zavracky R.H. Morrison and J. Krim, AVS 1999 National Symposium; *Viewing a Moving Contact*, J. Krim, B. Borovsky and B. Mason APS March 2000 Meeting, and AVS 2000 National Symposium *Vapor Phase Lubricants for MEMS Applications*, B. Borovsky, M. Abdelmaksoud and J. Krim, AVS 2000 National Symposium; Diffusion of TCP on Cr and Fe substrates, M. Abdelmaksoud, B. Borovsky and J. Krim, AVS 2000 National Symposium

Refereed Journal Articles

1. *Adsorption and Dissolution of TCP and TBBP in Fe and Chrome Surfaces: A quartz microbalance and Auger Spectroscopy study*, M. Abdelmaksoud and J. Krim, Tribology Letters, submitted
2. *Scanning Tunneling Microscope Measurements of the Amplitude of Vibration of a Quartz Crystal Oscillator*", B. Borovsky, B.L. Mason and J. Krim, J. Appl. Phys., in press
3. *Nanotribology: The Atomic-Scale Origins of Friction,* Millenium Volume of Surface Science on Frontiers in Surface and Interface Science, C.B. Duke and W. Plummer, eds. invited, in press
4. *Nanoscale Friction of Liquids at Interfaces*, T.S. Coffey, M. Abdelmaksoud and J. Krim, J. Physics Cond. Matt., Special Issue on Liquids at Interfaces, submitted, **invited**
5. *Friction on Macroscopic and Microscopic Scales*, J. Krim, Amer. J. Phys. Resource Letter, in preparation, **invited**
6. *Friction,* F. Family and J. Krim, McGraw-Hill Yearbook of Science and Technology 2000, p. *183 invited (Mcgraw-Hill, New York, 1999)*
7. *Fundamentals of Friction,* J. Krim, guest editor, MRS Bulletin, **23** (June 1998)
8. *Energy Dissipation in Interfacial Friction,* M.O. Robbins and J. Krim, in 7.

Proceedings Articles

9. *STM-QCM studies of Vapor Phase Lubricants*, B. Borovsky, M. Abdelmaksoud and J. Krim, "Nanotribology: Critical Assessment and Research Needs", S. Hsu, ed. (Kluwer, Dordrecht, 2000), **invited**
10. *Viewing a Moving Contact: A Scanning Probe and Quartz Crystal Microbalance Study of TCPand C60,* T.S. Coffey and M. Abdelmaksoud, B. Borovsky and J. Krim, in "*Fundamentals of Tribology and Bridging the Gap Between the Macro-and Micro/nanoscales:*, B. Bhushan, ed.
11. *Contact Resistance Modeling and Measurements of an Electrostatically Actuated Micromechanical Switch,* S. Majumder, N.E. McGruer, P.M. Zavracky, G.A. Adams, R.H. Morrison and J. Krim, MEMS symposium of ASME Meeting, Nov. 1998

(9) Honors/awards/other accomplishments:
Throughout the AFOSR award period, the PI's work has been widely recognized, as evidenced by the diverse nature of the invitations received for seminars, colloquia, and conference presentations and review articles. The PI is on the editorial boards of Tribology Letters and Tribology Transactions, and the Advisory Editorial Board of Surface Science. In addition to the invitation by

the Materials Research Society to be guest editor for a special issue on friction, the PI was selected for the distinguished visitor lecture series at Haverford College, PA, and the five-college Lecture series at
Holyoke College. She was named a Fellow of the American Vacuum Society in October 1999, a Fellow of the American Physical Society in March 2000 and a Sigma XI Distinguished Lecturer for 2001-2003. The July 22, 2000 feature article in Science News reports heavily on the PI's AFOSR-funded vapor-phase lubrication studies.